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Infrared (1-10 μ m) Atomic and Molecular Emission Signatures from Energetic Materials

ABSTRACT

Laser-induced breakdown spectroscopy (LIBS) is a powerful analytical technique to detect the elemental composition of solids, liquids, and gases in real time. For example, recent advances in UV-VIS LIBS have shown great promise for applications in chemical, biological, and explosive sensing. The extension of conventional UV VIS LIBS to the near-IR (NIR), mid-IR (MIR) and long wave infrared (LWIR) regions (\sim 1-12 μ m) offers the potential to provide additional information due to IR atomic and molecular signatures. In this work, a Q-switched Nd: YAG laser operating at 1064 nm was employed as the excitation source and focused onto several chlorate and nitrate compounds including KClO₃, NaClO₃, KNO₃, and NaNO₃ to produce intense plasma at the target surface. IR LIBS studies on background air, KCl, and NaCl were also included for comparison. All potassium and sodium containing samples revealed narrow-band, atomic-like emissions assigned to transitions of neutral alkali-metal atoms in accordance with the NIST atomic spectra database. In addition, first evidence of broad-band molecular LIBS signatures from chlorate and nitrate compounds were observed at \sim 10 μ m and \sim 7.3 μ m, respectively. The observed molecular emissions showed strong correlation with FTIR absorption spectra of the investigated materials.

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Block 13: Supplementary Note

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Infrared (1-12 μm) Atomic and Molecular Emission Signatures from Energetic Materials using Laser Induced Breakdown Spectroscopy

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ABSTRACT

Laser-induced breakdown spectroscopy (LIBS) is a powerful analytical technique to detect the elemental composition of solids, liquids, and gases in real time. For example, recent advances in UV-VIS LIBS have shown great promise for applications in chemical, biological, and explosive sensing. The extension of conventional UV-VIS LIBS to the near-IR (NIR), mid-IR (MIR) and long wave infrared (LWIR) regions ($\sim 1\text{-}12\ \mu\text{m}$) offers the potential to provide additional information due to IR atomic and molecular signatures. In this work, a Q-switched Nd: YAG laser operating at 1064 nm was employed as the excitation source and focused onto several chlorate and nitrate compounds including KClO_3 , NaClO_3 , KNO_3 , and NaNO_3 to produce intense plasma at the target surface. IR LIBS studies on background air, KCl , and NaCl were also included for comparison. All potassium and sodium containing samples revealed narrow-band, atomic-like emissions assigned to transitions of neutral alkali-metal atoms in accordance with the NIST atomic spectra database. In addition, first evidence of broad-band molecular LIBS signatures from chlorate and nitrate compounds were observed at $\sim 10\ \mu\text{m}$ and $\sim 7.3\ \mu\text{m}$, respectively. The observed molecular emissions showed strong correlation with FTIR absorption spectra of the investigated materials.

Keywords: Laser-induced breakdown spectroscopy, LIBS, infrared laser-induced fluorescence spectroscopy, explosives, energetic materials.

1. INTRODUCTION

Laser-induced breakdown spectroscopy (LIBS) has proven to be a versatile and sensitive probe for the detection and identification of many trace substances [1-5]. More recently, LIBS has shown great promise for sensing applications of chemical, biological, and explosive (CBE) materials [6-8]. LIBS is based on measuring the light emission from laser-induced plasma processes produced by short pulse excitation ($\sim 5\text{-}10\ \text{ns}$). Following the creation of a hot plasma, the investigated sample emits intense ultraviolet-visible-near infrared (UV-VIS-NIR) emission lines characteristic for electronic transitions of atoms, ions, and small molecular fragments (e.g. OH, CN) [9,10]. Important information concerning the identification, composition, and concentration of trace elements can be derived from the analysis of LIBS emission spectra. LIBS experiments are typically limited to spectral measurements in the UV-VIS-NIR region ($\sim 0.2\text{-}0.98\ \mu\text{m}$). It is well known, however, that molecules exhibit spectroscopic signatures in the long-wavelength IR region due to vibrational and rotational transitions. Therefore, an extension of LIBS to the IR region has the potential to provide additional information concerning the identification and classification of substances, which can augment results obtained from conventional LIBS measurements. In our previous work, we demonstrated mid-infrared (MIR, $3\text{-}5\ \mu\text{m}$) and long-wave infrared (LWIR, $4\text{-}12\ \mu\text{m}$) LIBS emission signatures from several solid state substances resulting from both atomic as well as molecular relaxation processes [11-13]. Very recently, we also reported the first distinct LWIR LIBS emission signatures in the $\sim 6\text{-}12\ \mu\text{m}$ region of several ammonium compounds due to dissociated and/or recombined molecular fragments [14]. In this work, we extended our IR LIBS studies to chlorate and nitrate based energetic materials including KClO_3 , NaClO_3 , KNO_3 , NaNO_3 and report on sample specific atomic and molecular emission signatures in the $1\text{-}12\ \mu\text{m}$ spectral region.

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2. EXPERIMENTAL CONSIDERATIONS

Powder samples of commercially available chlorate and nitrate compounds (Alfa Aesar) were pressed into tablets of nearly equal size using a hydraulic press. A schematic diagram of the experimental set-up for NIR, MIR and LWIR LIBS studies is shown in figure 1. The fundamental output wavelength (1064 nm) of a Q-switched Nd:YAG laser with 5 ns pulse width and repetition rate of 10 Hz was used to produce the LIBS plasma on the target sample. A liquid nitrogen cooled Indium Antimonide (InSb) detector was employed for the NIR and MIR (1-4.2 μm) spectral region, while a Mercury Cadmium Telluride (MCT) detector was utilized for LWIR (4.4-12 μm) detection. The laser beam was focused with a lens onto the sample surface leading to a beam diameter of ~ 1 mm. The energy per laser pulse on the sample surface was ~ 50 -75 mJ. The pressed samples were mounted onto a linear translation stage, which was controlled by a stepper motor controller. Samples were translated at a speed of ~ 1 mm/min, which ensured that the incident laser hit an unused target surface. It also reduced laser pulse fluctuation during the emission scan, which took ~ 12 minutes and covered a wavelength range of 1200 nm. The emission resulting from the plasma was collected by plano-convex CaF_2 or ZnSe lenses and focused onto the entrance slit of a 0.15m grating spectrometer. The spectrometer was equipped with gratings blazed at 2 μm (300 grooves/mm), 4 μm (150 grooves/mm), and 8 μm (75 grooves/mm). The slit width for measurements in the NIR and MIR regions was 25 μm , whereas a slit width of 2 mm was employed for the LWIR region. Different long pass filters were employed to block laser scattering and the short wavelength radiation of the emitted light. Time-resolved LIBS emission spectra were recorded using a boxcar average with a gate width of 15 μs and delay times of 16 μs (NIR, MIR) and 30 μs (LWIR), respectively.

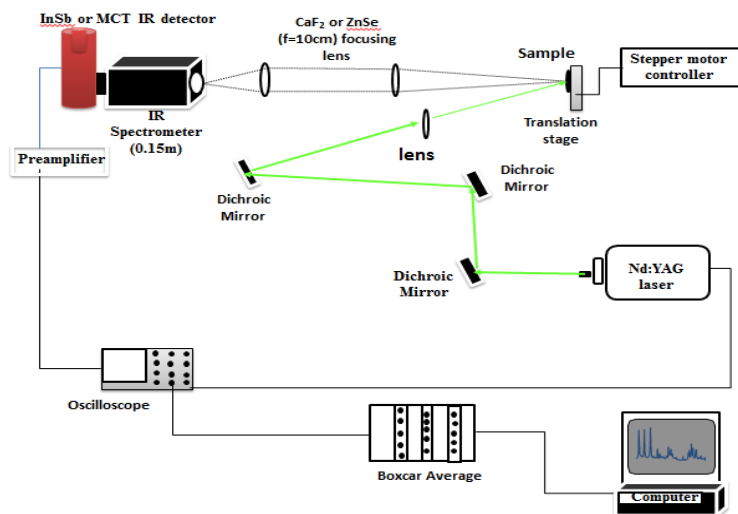


Figure 1: Experimental setup for NIR, MIR, and LWIR LIBS covering a spectral region from 1-12 μm .

3. RESULTS AND DISCUSSION

3.1 NIR and MIR LIBS Studies (1-4.5 μm)

Chlorate and nitrate compounds including KClO_3 , KNO_3 , NaClO_3 , NaNO_3 are known to be important oxidizing agents used in improvised explosive devices [7,15]. Fig. 2 depicts the NIR and MIR (1-4.5 μm) LIBS emission spectra observed from several potassium and sodium containing chlorates and nitrates. The LIBS spectra of KCl, NaCl, and background air are included for comparison. Under the given experimental parameters, background air did not reveal any distinct LIBS emission signatures. In contrast, intense atomic-like emission lines were detected from all potassium and sodium containing samples. The dominant lines for KClO_3 , KNO_3 , and KCl were centered at ~ 1.18 , ~ 1.26 , ~ 1.52 , ~ 2.72 , ~ 3.18 , ~ 3.77 and ~ 4.03 μm . Through comparison with the NIST atomic spectra database [16], these LIBS signatures can be assigned to atomic transitions of neutral potassium atoms as follows:

$3^2D_{5/2} \rightarrow 4^2P_{3/2}$, $5^2S_{1/2} \rightarrow 4^2P_{3/2}$, $4^2F_{5/2} \rightarrow 3^2P_{3/2}$, $5^2P_{1/2} \rightarrow 5^2S_{1/2}$, $5^2P_{1/2} \rightarrow 3^2D_{1/2}$, $4^2D_{5/2} \rightarrow 5^2P_{3/2}$, and $5^2G_{7/2,9/2} \rightarrow 4^2F_{5/2}$. For NaClO_3 , NaNO_3 , and NaCl the LIBS signatures were centered at ~ 1.85 , ~ 2.22 , ~ 2.38 , ~ 3.43 , ~ 4.05 μm and assigned to atomic transitions of neutral sodium atoms: $4^2F_{7/2} \rightarrow 3^2D_{5/2}$, $4^2P_{3/2} \rightarrow 4^2S_{1/2}$, $4^2D_{5/2} \rightarrow 4^2P_{1/2}$, $5^2S_{1/2} \rightarrow 4^2P_{3/2}$, and $5^2G_{7/2,9/2} \rightarrow 4^2F_{5/2}$ [16]. It is important to point out that under the given experimental conditions all potassium and sodium containing samples, respectively, exhibited very similar spectra, which limits their unique discrimination. Further time-resolved and high resolution NIR and MIR LIBS studies will be performed to identify sample specific atomic-emission signatures such as line ratios and decay transients.

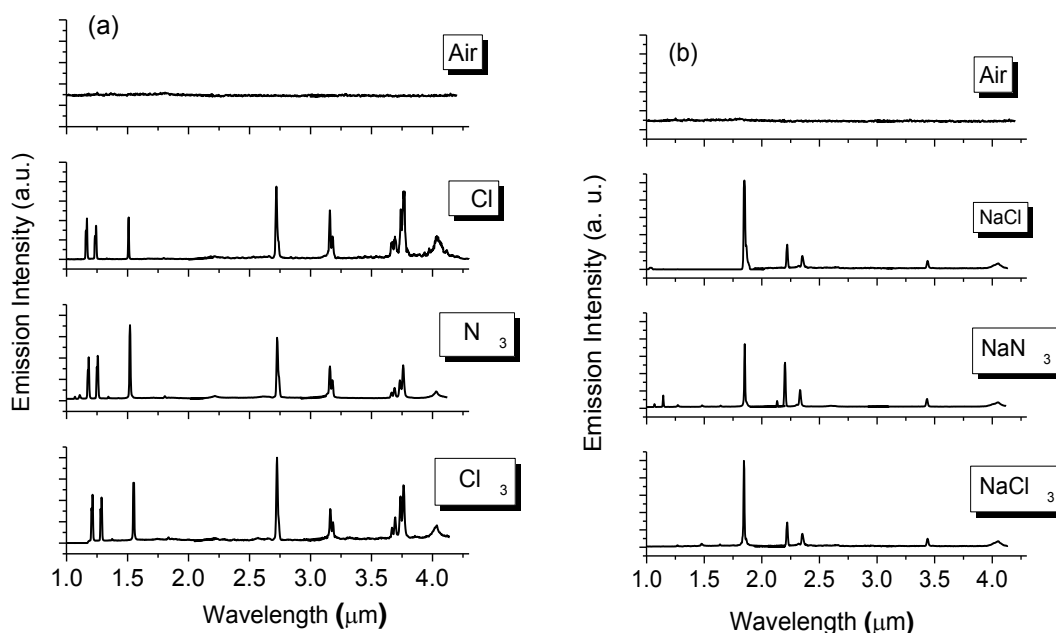


Figure 2: NIR and MIR LIBS emission spectra recorded under ambient conditions: a) potassium containing samples (KNO_3 , KClO_3 , KCl) and b) sodium containing samples (NaNO_3 , NaClO_3 , NaCl). The IR LIBS spectrum of air is included and did not reveal any significant emission signatures under the given experimental conditions.

3.2 LWIR LIBS Studies (4.5-12 μm)

The LWIR LIBS emission spectra (~ 4.5 - 12 μm) of the investigated chlorate and nitrate compounds measured under ambient conditions are depicted in Fig.3. The LIBS spectra of KCl , NaCl , and background air are included for comparison. The weak ~ 5.2 μm LIBS emission signature from air is close to the characteristic wavelength of the NO stretching mode (~ 5.3 μm) [14]. Similar to the NIR and MIR regions, the LWIR LIBS emission of air revealed only little structure. On the other hand, all potassium samples exhibited distinct LWIR emission signatures centered at ~ 6.3 , 7.5 , and 8.5 μm (Fig. 3a). A clear identification based on the NIST atomic spectra database was only possible for the LIBS emission at ~ 6.3 μm , which corresponds to the $6^2P_{5/2} \rightarrow 4^2D_{3/2}$ transition of neutral potassium atoms [16]. Several atomic emission signatures were also identified from sodium containing samples centered at ~ 4.66 , 5.01 , 5.42 , 7.42 and 9.11 μm and assigned to the following transitions of neutral sodium atoms: $7^2D_{3/2} \rightarrow 5^2F_{5/2}$, $5^2D_{3/2} \rightarrow 5^2P_{1/2}$, $5^2P_{3/2} \rightarrow 5^2S_{1/2}$, $8^2F_{7/2} \rightarrow 6^2D_{5/2}$, and $4^2P_{1/2} \rightarrow 3^2D_{3/2}$ [16]. Besides atomic LIBS emissions, it is important to point out that characteristic molecular emission structures were identified for chlorate and nitrate based materials. Broad LIBS emission features were observed for KClO_3 and NaClO_3 at ~ 10.5 μm , which can be assigned to the asymmetric stretching mode of the chlorate anion (ClO_3^-) [17]. For the nitrate compounds KNO_3 and

NaNO_3 , broad LIBS features were identified at ~ 7.2 and ~ 7.5 μm , respectively, which can be assigned to the asymmetric stretching band of the nitrate anion (NO_3^-) [14,18]. To further support the molecular assignments, the infrared absorption spectra of chlorate and nitrate samples are also shown in Fig. 3 (dotted lines) and indicate close agreement between molecular absorption and LIBS LWIR emission structures. It is noteworthy, that significant differences were also observed in the LIBS emission transients for atomic and molecular signatures. As shown in Fig. 4, the decay transient of the molecular chlorate signature at ~ 10.5 μm exhibited a slow decay component not found in the transient of atomic emission from neutral sodium atoms at ~ 7.5 μm . Further time-resolved LIBS studies are in progress to explore the differences in the decay dynamics of atomic and molecular IR LIBS emissions for possible sample identification.

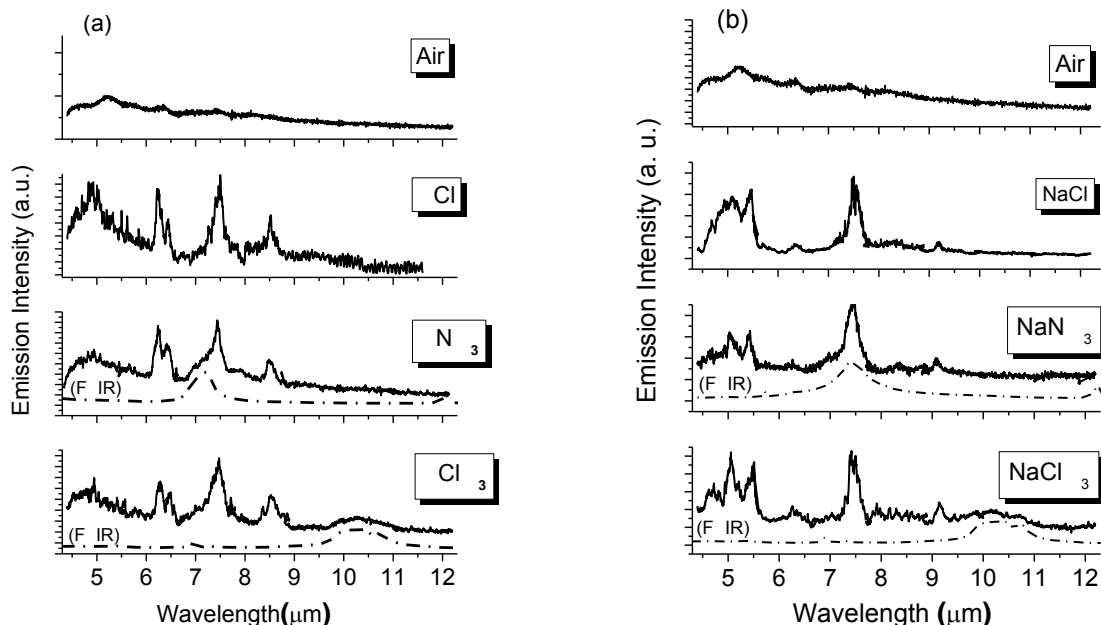


Figure 3: LWIR LIBS emission spectra recorded under ambient conditions: a) potassium containing samples (KNO_3 , KClO_3 , KCl) and b) sodium containing samples (NaNO_3 , NaClO_3 , NaCl). The IR LIBS spectrum of air is included for comparison. The FTIR absorption spectra of the corresponding chlorate and nitrate compounds are shown as dashed lines with characteristic molecular spectral features at ~ 7.2 μm (NO_3^-) and ~ 10.5 μm (ClO_3^-), respectively.

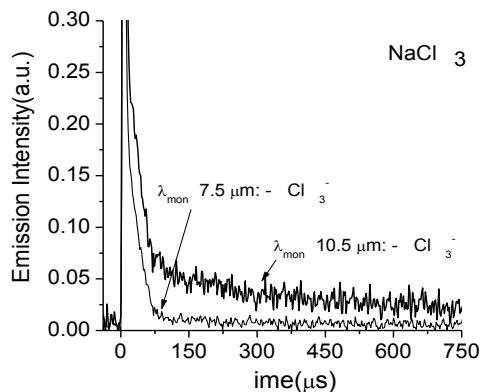


Figure 4: Example of LIBS emission transients for NaClO_3 monitored at atomic (sodium: ~ 7.5 μm) and molecular (chlorate: ~ 10.5 μm) LIBS signatures. The molecular LIBS emission revealed a significantly longer decay transient compared to the atomic LIBS emission.

3. CONCLUSIONS

We presented preliminary results of infrared (1-12 μm) LIBS studies on several chlorate and nitrate based energetic materials including KClO_3 , KNO_3 , NaClO_3 , and NaNO_3 . Intense IR atomic emission signatures were observed from all potassium and sodium containing compounds extending over a spectral region from ~ 1.1 to $9.1 \mu\text{m}$. These LIBS emission lines can be assigned to atomic transitions of neutral potassium and sodium atoms in agreement with the NIST atomic spectra database. Besides atomic signatures, first evidence of molecular LIBS emission signatures characteristic for chlorate and nitrate anions were observed at $\sim 10.5 \mu\text{m}$ and $7.2 \mu\text{m}$, respectively. These results support that IR LIBS can provide additional emission signatures for the identification and classification of substances, which can augment results from conventional UV-VIS LIBS.

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